Semiclassical calculation of collisional dissociation cross sections for N+N₂

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Dissociation and doubly differential cross sections are calculated for N+N₂ at near-threshold collision energies using a semiclassical wave packet method in which the vibrational motion of the molecule is treated quantum mechanically and the rotational and translational motions are treated classically. A three-bodied London–Eyring–Polanyi–Sato potential energy surface is used and results compared to those obtained using a purely repulsive power law potential. For a comparison of results, cross sections are also calculated using pure classical mechanics. © 2002 American Institute of Physics. [DOI: 10.1063/1.1504085]

I. INTRODUCTION

The collision-induced dissociation (CID) of the N₂ molecule by an energetic nitrogen atom is a process of importance in the upper atmosphere of Titan, a moon of Saturn, which has a nitrogen atmosphere. The energized nitrogen atoms produced by dissociation populate Titan’s atmospheric corona and can contribute to atmospheric loss. Essentially no atoms produced by dissociation populate Titan’s atmospheric composition of the N₂ molecule is treated quantum mechanically, and the vibrational motion of the molecule is treated quantum mechanically, while the rotational and translational motions are treated classically. A three-bodied London–Eyring–Polanyi–Sato potential energy surface is used and results compared to those obtained using a purely repulsive power law potential. For a comparison of results, cross sections are also calculated using pure classical mechanics.

II. THEORY AND CALCULATION

A. Semiclassical equation

To study the system A+BC→A+B+C we use the space fixed Jacobi coordinate system where r₁ is the vector joining atom B to C and r₂ is the vector joining atom A to the center of mass of molecule BC. The Hamiltonian for this system is given by

\[ H = -\sum_{i=1}^{2} \frac{\hbar^2}{2\mu_i} \left( \frac{\partial^2}{\partial r_i^2} + \frac{2}{r_i} \frac{\partial}{\partial r_i} + \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} \right) + \cot \theta_i \frac{\partial}{\partial \theta_i} \left( \frac{1}{\sin^2 \theta_i} \frac{\partial}{\partial \phi_i^2} \right) + V(r_i, \theta_i, \phi_i), \quad i=1,2, \]

where the vector r₁ is expressed in terms of spherical polar coordinates r₁, θ₁, and φ₁, θ₁, and φ₁ are the angles defining the orientation of the space fixed vectors r₁. \( \mu_1 \) is the reduced mass of the molecule BC and \( \mu_2 \) is the three-body reduced mass. If \( \Psi \) is the wave function associated with the Hamiltonian of Eq. (1), we can introduce a new wave function \( \psi \), given by

\[ \psi = r_1 \Psi, \]

so that the first derivative in \( r_1 \) in Eq. (1) is eliminated. The semiclassical Hamiltonian is then obtained by replacing the

\[ \hbar = \text{Planck’s constant} \]

\[ \mu_i = \text{Reduced mass of the molecule BC or the three-body reduced mass} \]

\[ r_i = \text{Distance between atoms} \]

\[ \theta_i = \text{Polar angle} \]

\[ \phi_i = \text{Azimuthal angle} \]

\[ V(r_i, \theta_i, \phi_i) = \text{Potential energy function} \]

\[ \cot \theta_i = \frac{\cos \theta_i}{\sin \theta_i} \]

\[ \mu_1 = \frac{m_A m_B}{m_A + m_B} \]

\[ \mu_2 = \frac{m_A m_B m_C}{2(m_A + m_B + m_C)} \]
variables associated with the translational and rotational motions in Eq. (4) with their respective classical counterparts, i.e.,

\[
\dot{H}_{\text{sc}} = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2} + \frac{P_{r_1}^2}{2\mu_2} + \sum_{i=1}^{2} \frac{1}{2\mu_i} r_i^2 \left( P_{\theta_i}^2 + \frac{1}{\sin^2 \theta_i} P_{\phi_i}^2 \right) + V(r_1, \theta_1, \phi_1), \quad i = 1, 2.
\]

In Eq. (3), the \( P_i \) are the classical momentum associated with \( r_2 \) and the orientation angles. The effective semiclassical Hamiltonian, which is defined as the expectation value of the semiclassical Hamiltonian, couples the classical and semiclassical degrees of freedom. It is given by

\[
\hat{H}_{\text{sc}} = \frac{\langle \psi | \hat{H}_{\text{sc}} | \psi \rangle}{\langle \psi | \psi \rangle} = \hat{H}_Q + \frac{P_{r_2}^2}{2\mu_2} + \frac{1}{2\mu_2 r_2^2} \left( P_{\theta_2}^2 + \frac{1}{\sin^2 \theta_2} P_{\phi_2}^2 \right) + \frac{1}{2\mu_1} \left( P_{\theta_1}^2 + \frac{1}{\sin^2 \theta_1} P_{\phi_1}^2 \right) \left( \frac{1}{r_1^2} \right)_{\text{eff}} + V_{\text{eff}}(r_1, \theta_1, \phi_1), \quad i = 1, 2,
\]

where

\[
\hat{H}_Q = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2},
\]

\[
\hat{H}_Q = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2} + \frac{1}{r_1^2} \left( \frac{\partial}{\partial r_1} \right)_{\text{eff}} \left( \frac{1}{r_1^2} \right),
\]

and

\[
V_{\text{eff}}(r_1, \theta_1, \phi_1) = \frac{\langle \psi | V(r_1, \theta_1, \phi_1) | \psi \rangle}{\langle \psi | \psi \rangle}.
\]

In the above equations \( \langle \cdot \rangle \) denotes integration over the quantal variable \( r_1 \).

\section*{B. Method of solution}

For the quantal part of the calculation the time-dependent Schrödinger equation is given by

\[
i\hbar \frac{\partial \psi(r_1, t)}{\partial t} = \left[ -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial r_1^2} + \frac{1}{2\mu_1} r_1^2 \left( \frac{P_{\theta_1}^2}{\sin^2 \theta_1} \right) \right] \psi(r_1, t) + V(r_1, \theta_1, \phi_1) \psi(r_1, t).
\]

During the propagation of the wave function, the variables \( r_2, \theta_i, \) and \( \phi_i, \) \( i = 1, 2 \) and the momenta, \( P_{\theta_1} \) and \( P_{\phi_1} \), were passed from the classical calculation and remained constant for each time step \( \Delta t \). The wave packet propagation was carried out using the symmetrized split operator (SSO) fast Fourier transform (FFT) method and a finite grid, which is described briefly in the Appendix. The initial wave function \( \psi(r_1, t=0) \) in the vibrational state \( v \) was taken as a Morse oscillator wave function. Because we will use the population of the bound states below, we eliminate the reactive and dissociative contributions to the wave function by introducing an absorbing potential,

\[
V_{\text{abs}} = \begin{cases} -i V_0 \Delta t (r_1 - r_{\text{abs}}) / \hbar \Delta r_{\text{abs}}, & r_{\text{abs}} \leq r_1 \leq r_{\text{abs}} + \Delta r_{\text{abs}} \\ 0, & r_1 > r_{\text{abs}}, \end{cases}
\]

where \( V_0 \) is the height and \( \Delta r_{\text{abs}} \) the width of the absorbing potential and \( r_{\text{abs}} \) is its location on \( r_1 \), which is placed sufficiently far away from the interaction region. This procedure also prevents any reflection at the boundaries that arise naturally in the SSO FFT method.

The classical equations of motion, given by

\[
\dot{\theta}_1 = \frac{P_{\theta_1}}{\mu_1} \left( \frac{1}{r_1^2} \right)_{\text{eff}}, \quad \dot{\phi}_1 = \frac{P_{\phi_1}}{\mu_1 \sin^2 \theta_1} \left( \frac{1}{r_1^2} \right)_{\text{eff}}, \quad \dot{r}_2 = \frac{P_{r_2}}{\mu_2},
\]

\[
\dot{P}_{\theta_2} = \frac{P_{\phi_2} \cos \theta_2}{\mu_2 r_2^2} - \frac{\partial V_{\text{eff}}(r_1, \theta_1, \phi_1)}{\partial \theta_2},
\]

\[
\dot{P}_{\phi_2} = \frac{P_{\theta_2} \sin \theta_2}{\mu_2 r_2^2} - \frac{\partial V_{\text{eff}}(r_1, \theta_1, \phi_1)}{\partial \phi_2},
\]

were integrated, for each randomly chosen impact parameter, \( b \), set of orientation angles, \( \theta_1 \) and \( \phi_1 \), and initial center of mass energy, using a fourth-order predictor corrector method. Angles \( \theta_1 \) and \( \phi_1 \) were chosen in the range \( 0 \leq \theta_1 \leq \pi \) and \( 0 \leq \phi_1 \leq 2\pi \), respectively. The initial position of the atom A was chosen to lie along the \( z \) axis at an initial distance \( r_2 \) sufficiently large in order for the interaction potential to be negligible. In those cases for which the collision is primarily dissociative or reactive the calculation was terminated when the norm of the wave function remaining on the grid was negligible. Otherwise the trajectory was terminated when the distance between the atom and the center of mass of the molecule is larger than \( r_{\text{max}} \), where we chose \( r_{\text{max}} = 8 \text{ Å} \).

Due to the lack of accurate \( ab \text{ initio} \) potential energy surfaces for the system \( N + N_2 \), we used a London–Eyring–Polanyi–Sato potential energy surface, calculated by Lagana et al. This is likely accurate in describing the three-body affects at long range but is probably not very accurate for close collisions between atoms, as discussed later.

The simultaneous evaluation of the quantal and classical degrees of freedom is performed in the following way. After
C. Transition probabilities and cross sections

The probability of dissociation is calculated by first projecting the final wave function onto each asymptotic vibrational state to obtain the vibrational transition probabilities, i.e.,

\[ P_{v \rightarrow v'} = \left| \int \psi(r_1, t = \infty) \phi_{v'}(r_1) dr_1 \right|^2, \quad (12) \]

where \( \phi_{v'}(r_1) \) is the Morse oscillator wave function for vibrational state \( v' \). If a sufficient number of vibrational states are included, then the probability of the collision being nondissociative and nonreactive, \( P_{\text{NDR}} \), is obtained by adding together all the vibrational transition probabilities,

\[ P_{\text{NDR}} = \sum_{v'}^\infty P_{v \rightarrow v'}, \quad (13) \]

where \( v_{\text{max}} \) is the maximum vibrational state. To determine if a reaction has taken place (i.e., \( A + BC \rightarrow AB + C \) or \( A + BC \rightarrow AC + B \)) we calculate the kinetic energy and the potential energy both between atoms \( A \) and \( C \) and between atoms \( A \) and \( B \). If the kinetic energy plus the potential energy is less than zero for either case, then a reaction has taken place. Due to the presence of the absorbing potential we place a limit on the maximum separation of the BC molecule, \( r_{\text{max}} \). Therefore when \( r_1 > r_{\text{max}} \), the calculation ends. We chose \( r_{\text{max}} = 8 \) Å which is large enough to make a good estimate of the final positions and total energies between all three atoms but is small enough to provide accurate results for the number of grid points used in the FFT calculation. For a given orientation and impact parameter, \( P_R \) is either 1 or 0, whereas \( P_{\text{NDR}} \) can range anywhere between 0 and 1. Therefore we estimate the probability of dissociation, \( P_D \), as follows; if \( P_R = 1 \) we set \( P_D = 0 \), otherwise

\[ P_D = 1 - P_{\text{NDR}}. \quad (14) \]

This method ensures that \( P_D \) is never less than zero. The total integrated cross section for dissociation is obtained by

\[ \sigma_D = \int_0^{b_{\text{max}}} b P_D db, \quad (15) \]

where \( b_{\text{max}} \) is the maximum value of the impact parameter \( b \) and \( P_D \) is the probability of dissociation averaged over initial orientation. For a more detailed analysis of the system we calculate also the doubly differential cross section, which is given by

\[ \frac{d^2 \sigma}{d\Omega de} = 2 \pi \sum_i^n P_i(e, \chi) b \Delta b \frac{2 \mu_1 D_e}{\hbar^2 \beta^2}, \quad (16) \]

where \( P_i(e, \chi) \) is the probability of the scattering angle being in the range \( \chi - \Delta \chi/2, \chi + \Delta \chi/2 \) with final energy in the range \( (e - \Delta e)/2, e + \Delta e/2 \). This is averaged over the number of initial orientations for a given impact parameter \( b_i \). Here \( N \) is the total number of impact parameters and \( e \) is the energy in the center of mass of the atom–molecule system. For this set of collision partners the net energy transfer from the incident \( N \) to the molecule is \( T = 1.5[\epsilon_0 - \epsilon] \), where \( \epsilon_0 \) is the initial energy in the center of mass.

III. RESULTS AND DISCUSSION

Since the dissociation threshold energy of \( N_2 \) is 9.91 eV, the dissociation cross sections were calculated at energies, \( \epsilon_0 \), between 9 and 40 eV for the ground vibrational state \( v = 0 \). The wave function was propagated on a grid of 1024 discrete points and the maximum value of the \( N_2 \) separation was 8.0 Å and the minimum value 0.3 Å. Larger and smaller values for the grid length and the maximum \( r_{\text{max}} \) were tested to find the best values. The maximum vibrational quantum number was calculated using the semiclassical approximation,10

\[ \left( \frac{v + \frac{1}{2}}{2} \right)^2 = \frac{2 \mu_1 D_e}{\hbar^2 \beta^2}, \quad (17) \]

where \( D_e = 9.91 \) eV is the dissociation energy and \( \beta = 2.689/\text{Å} \), and was found to be \( v_{\text{max}} = 67 \). For the total dissociation cross sections the maximum value for the impact parameter was taken to be 1.5 Å and for the differential cross sections was chosen to be 4.0 Å. For each impact parameter we integrated trajectories for 100 random initial orientations for each energy and we chose \( \Delta b = 0.05 \) Å. For the absorbing potential we chose \( V_0 = 100 \text{ eV} \) and \( \epsilon_{\text{abs}} = 1.0 \text{ Å} \).

In Fig. 1 we compare how the probability of dissociation and reaction vary with impact parameter \( b \) for the semiclassical and classical calculation using the LEPS PES at the center of mass energy 30 eV. Using the LEPS PES at small
impact parameters (<0.5 Å) the probability of reaction dominates over that of dissociation but as the impact parameter increases so too does the probability of dissociation until the peak at about 1 Å.

Collisional dissociation cross sections are shown in Fig. 2 for center of mass energy varying between 9 and 40 eV. These are carried out using the semiclassical method described above and a classical molecular dynamics calculation both using the LEPS PES potential. Also shown in this plot is the classical calculation using the pair potentials obtained by Johnson et al.¹ For energies greater than 20 eV it can be seen that the classical and semiclassical results agree well for the LEPS PES. However, on approaching the dissociation threshold energy (9–20 eV) the semiclassical approximation predicts more dissociation than the classical. The pair potentials are in the form of a repulsive power law potential, given by

$$V_n = \frac{C_n}{r^n},$$

where $r$ is the separation of the atoms and $C_n$ and $n$ are obtained from data extracted from dissociation cross sections for O+N$_2$.¹ The differences between the results of the LEPS PES and those of the power law potentials are primarily due to the three-body terms present in the LEPS PES. That is, as the incident N approaches, the molecule becomes highly distorted. Because the cross section is very sensitive to the details of the potentials in this energy range, accurate potentials are needed.

Finally, in Fig. 3 the semiclassical doubly differential cross sections are given for a range of final energies plotted against the center of mass scattering angle $\chi$.

**IV. CONCLUSIONS**

We have calculated the dissociation cross sections, the reaction cross sections, and the doubly differential cross sections for N+N$_2$ for energies in the center of mass of the N + N$_2$ system, $\epsilon_0$, in the range 9–40 eV using a semiclassical method. Because a goal was to better describe the dissociation probability near the threshold region, we used a three-body model potential that can roughly describe the ground state of N$_3$. This differs considerably from the pair potentials used earlier. For comparison to our semiclassical calculations we also carried out fully classical calculations using the three-body potential.

We find that in the region studied the pair potentials fail dramatically both in describing the dissociation probability with impact parameter and the total dissociation cross sections. However, using the three-body potential constructed from Morse potentials fails at large energy transfers. Therefore, in the region where the repulsive part of the potential dominates (>~40 eV), an appropriate description of the repulsive part of the potential is needed. In this velocity region, excitations within the ground state multiplet should also be included.

Although our goal was to study collisional dissociation in Titan’s upper atmosphere, we found surprisingly large reaction probabilities for the N+N$_2$ system. However, our cross sections for reaction plus dissociation channels are the most reliable. The separation into reaction and dissociation
cross sections requires that we estimate the position of the dissociated atoms with respect to the incident N. It should also be noted that since a finite grid is used it is difficult to accurately calculate the highly excited vibrational eigenstates up to the dissociation limit. Another method would be to calculate the flux and integrate it to obtain the probability that the molecule has dissociated. It is seen that for both the dissociation and the reaction cross sections, there is rough agreement of the classical result with the semiclassical calculation. Because the semiclassical method allows dissociation when the average vibrational state is below the dissociation limit, the semiclassical dissociation cross section is larger than the classical result at the lowest energies as expected. In treating low-energy collisions, the most important improvements that can be made are the use of a better potential surface that accurately treats both the binding and the repulsive regions and, where reactions are important, a fully quantal calculation. The cross sections calculated here are now being incorporated in a particle transport code\textsuperscript{1} to describe the heating and loss of Titan’s upper atmosphere in preparation for the arrival of the Cassini spacecraft at Saturn (see Fig. 4).

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**APPENDIX: THE SPLIT OPERATOR FAST FOURIER TRANSFORM METHOD**

The time propagation of the wave function $\psi(r_1, t)$ is carried out using the symmetrized split operator fast Fourier transform method proposed by Fleck et al.\textsuperscript{11} The following is based on the description by Feit et al.\textsuperscript{12}

If at time $t=t_0$ the initial wave function $\psi(r,t_0)$ is known on the grid $r=[r_{\text{min}}, r_{\text{max}}]$, where $r_{\text{min}}$ is the minimum value of $r$ and $r_{\text{max}}$ is the maximum, then the solution of the wave function having advanced through a time step $\Delta t$ is given by

$$\psi(r,t_0+\Delta t)=\exp\left[-i\left(\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V(r)\right) \frac{\Delta t}{\hbar}\right] \psi(r,t_0).$$

(A1)

If $\Delta t$ is sufficiently small then this can be approximated by

$$\psi(r,t_0+\Delta t)=\exp\left(-i\frac{\hbar}{4\mu} \frac{\partial^2}{\partial r^2}\right) \exp\left(-i\frac{\hbar}{4\mu} V(r)\right) \psi(r,t_0),$$

(A2)

which is the symmetrized split operator form.

The solution to the first term in Eq. (A2),

$$\exp\left(-i\frac{\hbar}{4\mu} \frac{\partial^2}{\partial r^2}\right),$$

is obtained by using the band-limited Fourier series representation,

$$\exp\left(-i\frac{\hbar}{4\mu} \frac{\partial^2}{\partial r^2}\right) \psi(r,t_0) = \sum_{n=-N/2}^{N/2} \psi_n(t_0+\Delta t)e^{2\pi in j/N},$$

(A3)

where

$$\psi_n(t_0+\Delta t) = \left(\frac{1}{N} \sum_{j=0}^{N-1} \psi_0(r_{\text{min}}+\Delta r_{j},t_0)e^{-2\pi in j/N}\right) \times \exp\left[-i\frac{\hbar}{4\mu} \frac{2\pi n}{L_0}\right]^2,$$

(A4)

In Eq. (A4), $L_0$ is the length of the grid $[r_{\text{min}}, r_{\text{max}}]$, $N$ is the number of grid points, and $\Delta r=L_0/N$. The efficiency of this procedure can be increased by using a fast Fourier transform algorithm in evaluation of Eqs. (A3) and (A4). Accurate results are obtained by choosing $L_0$ large enough so that the amplitude of the wave function is negligible at the grid ends and by choosing $\Delta r$ small enough to accommodate the spatial bandwidth of the wave function. The time step $\Delta t$ must also satisfy the condition

$$\Delta t < \frac{\hbar}{\Delta V_{\text{max}}},$$

(A5)

where $\Delta V_{\text{max}}$ is the difference between the highest and lowest potential values in the Franck–Condon region.